

# Working Group on Nanostructures and Special Opportunities in Semiconductors

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## 1. Introduction

Reduced dimensionality and nanostructures, in particular, are themes cutting across several of the reports of the working groups. Nanostructures are low-dimensionality material systems whose size is intermediate between that of atoms or molecules and that of bulk solids. (A nanostructure may be defined as any structure with at least one dimension of order 1 nm.) These novel materials, which modern techniques of synthesis and processing can now produce, have physical and chemical properties that are different from those of the bulk parent compounds and also from those of the constituent atoms and molecules. The properties are strongly dependent upon size and shape. These properties are controlled by quantum size effects, altered thermodynamics and, modified chemical reactivity.

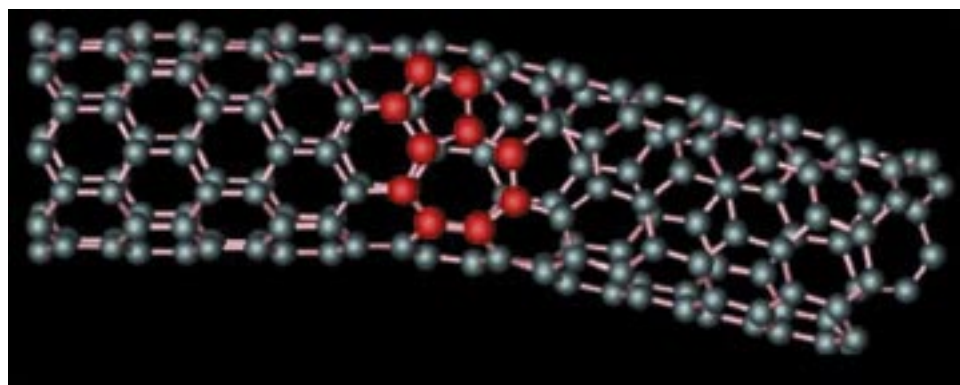
Generally, the interest in understanding nanostructures is focused on the ability to modify materials so that they have properties unavailable in bulk-process materials. These include the electronic, structural, magnetic, optical, superconductive, transport, ferroelectric, and electron-lattice properties of the materials. Examples of nanostructures include quantum dots; nanocrystals and clusters; large molecules and buckyballs; onions; nanotubes, nanoropes, and nanoribbons; and a variety of materials with reduced geometry. They can be free standing, capped by protective layers, or embedded in matrices.

Nanoscience is evolving at a fast pace, and the number of projects in nanoscience research being undertaken by physicists, chemists, materials scientists, and biologists is increasing rapidly. Because this area of inquiry is concerned with a length scale that is of interest to all these disciplines, there are excellent opportunities for collaboration. In addition to the basic scientific questions of how materials behave at the nanometer scale, research in nanostructures opens new opportunities for the design and optimization of properties for specific technological purposes and applications.

An understanding of electronic structure in small confined geometries has obvious importance in electronic, optoelectronics, and memory devices (Figure 1). Structural properties of materials and knowing how to influence their bulk properties are of interest. In addition, the general area of understanding inorganic structures related to biological materials is of great importance.

This working group considered the possible applicability of the ALS to probing these properties of nanostructures on, or beyond, the performance level of currently available techniques. (Examples of currently available techniques are scanning probes, various means of studying transport, lasers, conventional spectroscopy with soft and hard x-rays, electron microscopy, and optical reflection and absorption.)

In addition to nanoscale studies of materials, the ALS offers novel opportunities for studies of small material samples at extreme hydrostatic pressures in diamond-anvil cells over a wide range of photon energies (infrared through soft x-ray). The ALS also enables tunable-ultraviolet studies of wide-bandgap materials, especially the Group III nitrides. Scientific opportunities in the infrared (IR)-visible-ultraviolet (UV) continuum are especially attractive for two reasons: first, only a simple, inexpensive beamline is needed; and second, the Berkeley location of the ALS offers excellent opportunities for collaboration with researchers in many different disciplines.



*Figure 1. A metal-semiconductor junction of carbon nanotubes. Theoretical calculations [L. Chico, V. H. Crespi, L. X. Benedict, M. L. Cohen, and S. G. Louie, Phys. Rev. Lett. 76 (1996) 971] show that a pair of five- and seven-membered rings changes the helicity of the carbon nanotube and thus joins a metallic segment to a semiconducting segment to form a nanoscale Schottky barrier. [See also "Mixing Nanotube Structures to Make a Tiny Switch," R. F. Service, Science 271(1996) 1232.] Recently there has also been experimental observation of such on-tube device behavior by A. Zettl's group at the University of California, Berkeley. [Figure courtesy of the research groups of M. L. Cohen and S. G. Louie at the University of California, Berkeley.]*

## 2. Opportunities in Nanostructures

### 2.1 Tailored Properties

Franz Himpsel (leader), University of Wisconsin–Madison; Christoph Bostedt, Lawrence Berkeley National Laboratory; Wolfgang Eberhardt, Forschungszentrum Jülich; Steven G. Louie, University of California Berkeley; Jan Luening, IBM Almaden Research Center; Bruno Reihl, Paul Scherrer Institute; Tony van Buuren, Lawrence Livermore National Laboratory.

#### 2.1.1 What Are the Interesting and Important Scientific Questions?

We earlier defined a nanostructure as any structure with at least one dimension of order 1 nm, whatever its extent in the other two dimensions. However, conceptually there are two types of nanostructures. One type of structure is based on confining electrons by changing the boundary conditions. The size of such an object is of the same order as the wavelength of an electron. The other type is even smaller and may be viewed as a large assembly of atoms in which not only the boundary conditions but also the Hamiltonian differ from those of a bulk material. It may be thought of as an object consisting only of interfaces with no bulk behind them. This interface nature has ramifications, such as optical properties determined by surface states and many-body effects, that give such materials different properties than bulk materials that are nanoscale in only one dimension.

The lower dimensionality of some structures (e.g., one-dimensional lines) causes qualitative changes in the way electrons behave. For example, in one dimension, the Fermi-liquid model does not apply, and electrons can separate into charges and spins. In essentially zero-dimensional objects that are confined in all three directions and are of size comparable to an electron wavelength, the electronic structure is a function of the number of atoms and electrons in the system.

In nanostructures, one can exert a level of control over structural detail (e.g., electron wavefunctions) that is not available in bulk materials. An example is making a  $C_{60}$  (or other fullerene) film instead of a diamond or graphite film. Much of the appeal of making nanostructures is the ability to tailor a material's properties by manipulating wavefunctions. One way to do this is by confining electrons to physical dimensions comparable to their de Broglie wavelength (Figure 2). This occurs in quantum wells, for example.

Even structures larger than a quantum well, such as clusters, can be dominated by electrons at surfaces and interfaces that are in completely different electronic states than would be encountered in bulk materials. Covalent bonding can change to metallic bonding and vice versa. Screening and other many-body electronic interactions can also dramatically change.

Which electrons are relevant? For some properties, the ones within  $kT$  of the Fermi level are of greatest importance—for example, in a Stoner-criterion model for ferromagnetism and in the conventional formulae for the critical temperature  $T_c$  of superconductors. For other aspects, such as optical properties, electron states at the band edges and multi-electronic excitations like plasmons are the important contributors. This is a key difference between metals and semiconductors. For the smaller types of clusters, the full orbital structure will become important. Strain and local crystallography can be used to tune properties of embedded nanostructures.

These are questions of great potential importance to science and technology. By tailoring electronic structures, we can control the behavior of materials, including their magnetic, optical, superconductive, transport, and other physical properties. For example, the first nanostructures created by man (as we know in retrospect) were stained-glass windows and other colored glasses. A recent high-technology example is the giant magnetoresistance (GMR) technology used for the latest hard-disk read

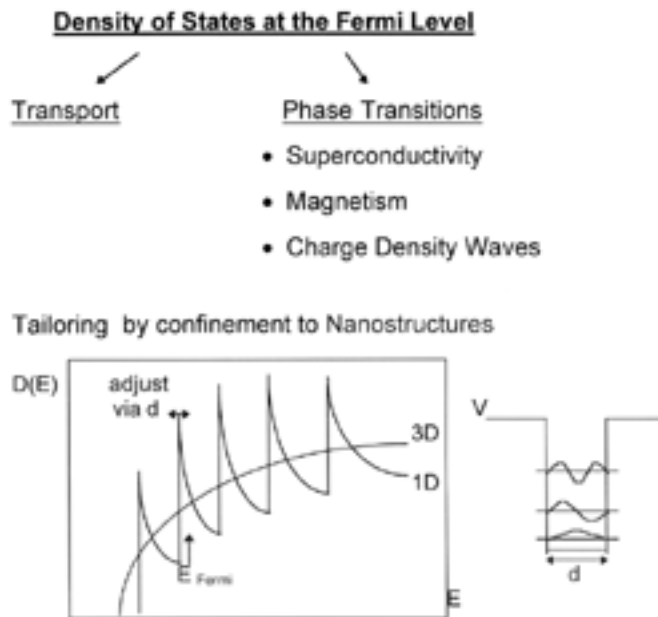


Figure 2. The density of electron states at the Fermi level determines many properties of materials. By physically confining electrons to small areas in one or more dimensions (nanostructures), the density of states, and thus the materials properties, can be tailored. [Figure taken from F. J. Himpsel, J. E. Ortega, G. J. Mankey, and R. F. Willis, *Advances in Physics* **47** (1998) 511.]

heads (Figure 3). The gate oxide in silicon MOSFETs, as used in most integrated circuits, is another example. A third example is the quantum-well laser that has become ubiquitous in modern life. Nanostructures will be even more important in future devices that are based on single-electron switching. Chemical reactivity in the most general sense is an electronic-structure effect. And we merely note in passing that the Working Group on New Directions in Surface and Interface Science is reporting on heterogeneous catalysis, which occurs on nanostructured surfaces.

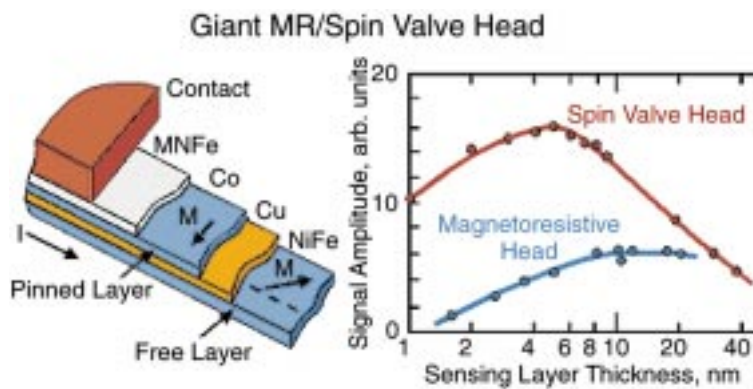


Figure 3. Structure of a giant-magnetoresistance spin-valve read head for hard disks. It exemplifies the way that nanostructures are becoming ever more important as enabling technologies behind the items of everyday life. [Figure courtesy of Ed Grochowski and Virgil Speriosu, IBM.]

### 2.1.2 What Role Can the ALS Play in Advancing the Field?

Some critical applications of synchrotron radiation in nanostructure science are:

- Identifying the atomic structure of interfaces, wires, and nanoparticles. Soft-x-ray scattering reveals just the right Fourier components, the ones that are most relevant to the confinement of electrons. The ALS is particularly appropriate because it readily produces radiation whose wavelength is about the size of nanostructures. Particularly useful in soft-x-ray scattering are the L edges of the magnetic metals in the IIId column of the periodic table; these edges make it possible to determine the atomic and magnetic structure of interfaces, in element-sensitive fashion, via resonant x-ray scattering.
- Determining the relevant electronic states at the Fermi level by high-resolution photoemission spectroscopy. Here again, resonant photoemission at the M edge of the IIId metals and the d-to-f resonance of the rare earths and actinides allows experimenters to achieve elemental specificity.
- Determining magnetism of nanostructures via soft x-ray magnetic circular dichroism (XMCD). A critical issue will be the sensitivity of XMCD to sub-monolayer quantities and to buried interfaces. One suggestion is to use XMCD in conjunction with core-level fluorescence spectroscopy. XMCD can provide semi-quantitative data on the orbital and spin moments, separately for each element, in nanostructures. This is impossible with traditional techniques, such as neutron scattering, that require a macroscopic amount of material.

Soft-x-ray emission spectroscopy as an experimental technique benefits tremendously from the brightness advantage of a third-generation synchrotron light source such as the ALS. This technique is ideally suited to studying the electronic structure of nanostructures on surfaces, embedded clusters, clusters with a ligand shell, or buried interfaces. The experiments that can be performed include measuring energy levels and band offsets that are not accessible to traditional optical experiments.

All of these techniques have thus far been applied to arrays of nanostructures all the same size. It seems likely that the ALS will soon have unique spectromicroscopy techniques that can examine individual nanostructures.

## 2.2 Synthesis/Fabrication of Nanostructures and Architectonic Materials

Stan Williams (leader), Hewlett-Packard Laboratories; Jason Guo, Stanford University

### 2.2.1 Scientific Issues in Synthesis/Fabrication

New functionality that depends upon size and shape emerges as materials are prepared with nanometer dimensions. These new characteristics may involve electronic, optical, structural, chemical, or even biological properties of matter. Quantum confinement strongly perturbs the energy level structure of semiconductors, metals and ferroelectrics, and can enable their properties to be tuned to optimize them for particular applications. Elemental carbon can be made semiconducting, metallic or even superconducting, depending upon the atomic structure of the individual moieties (chemical states) and the doping of aggregate configurations. Organic nanostructures may be created that can transport medicines through the bloodstream or even through cell walls to target specific organs or diseases. Composite nanostructures that combine two or more functionalities provide fascinating possibilities for totally original applications.

Each class of material presents unique challenges for the fabrication of nanostructures. For most of the systems currently under consideration, one ideally wants to manufacture large amounts of nanostructures with essentially identical sizes and shapes (Figure 4). For the most part, this involves



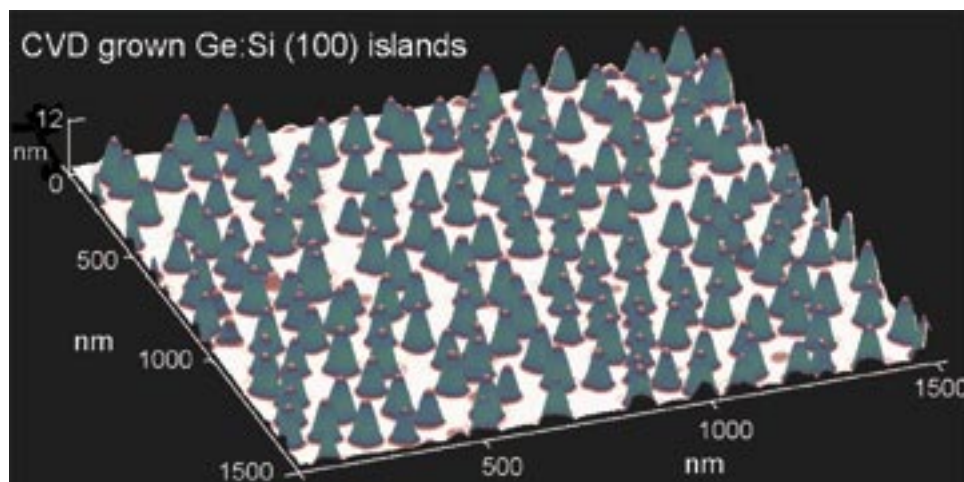


Figure 4. A thick film grown by CVD and measured ex-situ by atomic force microscopy (AFM) shows very good size uniformity. [Figure courtesy of the research group of Stan Williams, Hewlett-Packard Laboratories.]

chemical syntheses that are sometimes described as “self-assembling” if they can be designed to produce the desired products simply by the control of reaction conditions. It may also be desirable to fabricate structures that can change their size or shape predictably under the influence of an external stimulus. For some applications, independent nanostructures will be sufficient, but for many others it will be necessary to position specific nanostructures at well-defined locations on a substrate or to create larger-scale constructions to form architectonic (purposely designed) materials that may in turn be a part of a larger device or system. In these latter cases, the connectivity of the superstructures will be extremely important, and if connectivity is achieved by controlling the interaction chemistry of the nanostructures, the process is known as self-organization.

As with any synthesis process, there must be rapid feedback between the steps of the synthesis and the characterization of the intermediates, as well as the final target structure. Ideally, the characterization procedure provides direct physical or chemical information on the desired properties of the nanostructures—information that can be used to select or adjust synthesis conditions and that also yields data that can improve the theoretical understanding of the process for planning future syntheses. For example, at the present time, those who synthesize nanocrystal semiconductors use optical absorption and fluorescence to characterize their materials, since often the optical properties are the most relevant. The positions of peaks in the spectra are related to the size of the nanocrystals, and the width of the peaks can contain information about the size dispersion. However, other materials do not have such convenient optical signatures, or the signatures may be ambiguous, and for those a direct determination of the size, shape and arrangement of the nanostructures is necessary. For these systems, direct imaging with either transmission electron microscopy or scanning probe microscopy are the primary methods currently employed (Figure 5). However, both techniques are fairly slow, and the analysis of the data can be labor-intensive and cumbersome.

### 2.2.2 The Role of the ALS

The ALS can play a very important role in optimizing procedures for synthesizing and organizing nanostructures. The scattering of soft x rays, which have wavelengths on the order of nanometers, depends very strongly on the size, shape, and connectivity of nanostructured samples and automatically provides information on averaged properties of the scattering target. Also, the extremely low emittance of the ALS allows the use of beams with very high intensity with small spot sizes. These are

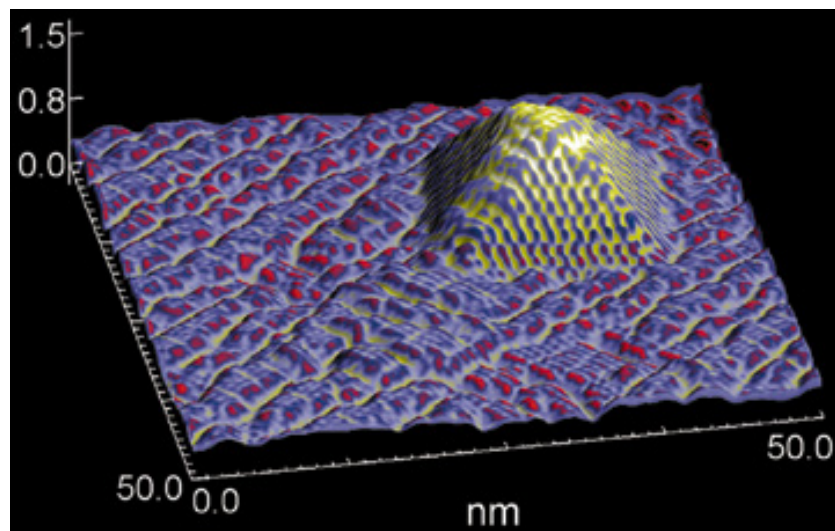


Figure 5. High-resolution scanning tunneling microscope (STM) image made under ultrahigh vacuum after growth of a 4- $\mu\text{m}$ -thick film of germanium on a silicon (001) surface. [Illustration courtesy of the research group of Stan Williams, Hewlett-Packard Laboratories.]

necessary to analyze large combinatorial libraries of nanostructures in reasonable times. Using techniques currently under development for drug and materials discovery, it will be possible to prepare substrates that hold more than 100,000 discrete samples, each of which is of order 10  $\mu\text{m}$  square. Using a soft x-ray scattering system at ALS, it will be possible to collect forward- and back-scattering data on all of these samples and utilize a computer-automated analysis and sorting process to rapidly identify promising leads from the library. Depending on the samples and the properties for which one is screening, the soft x-ray scattering can be made specific to elements and even to chemical states by using radiation at a particular absorption edge, as discussed in Section A. The scattering can also be made sensitive to other properties, such as dichroism. After selecting the most interesting samples from the library, they can then be examined at or near the individual nanocrystal level using high-resolution photoelectron spectroscopy and other techniques, depending on the properties of interest. Again, the soft x rays in the photon-energy range from 100 eV to 1000 eV are ideal for limiting the collected photoelectrons from the outermost nanometer or so of the structures.

In order to accomplish these objectives, new end stations and sample-handling techniques will be required. In general, an end station cluster that can handle large wafers will be required for the soft x-ray scattering and other techniques. Also, sample transfer and cleaning techniques will be required. In general, the syntheses and library construction will be performed at a remote location, perhaps even in a different country. The samples then need to be transported to the ALS in a clean environment, perhaps in a container known as an ultrahigh-vacuum suitcase. Such suitcases need to be compatible with the ALS end station, so that samples can be transferred into them without exposure to atmosphere. In addition, it may be necessary to clean the samples once they have been introduced into the end station, to remove some contaminants. Careful thought in the design of end stations and sample handling can make the ALS accessible to a very large community of scientists, who in principle could send their samples to the ALS by means of an overnight-shipping company and receive their data through the World Wide Web. This makes possible the screening of millions of possible systems per year in each of a large number of laboratories. Such analytical feedback would have a profound effect on the progress of nanostructure and architectonic materials synthesis.

## 2.3 Embedded Nanostructures and Synergy between the ALS and the National Center for Electron Microscopy (NCEM)

Uli Dahmen (leader), Lawrence Berkeley National Laboratory; John Spence, Arizona State University

### 2.3.1 Properties of Embedded Nanostructures

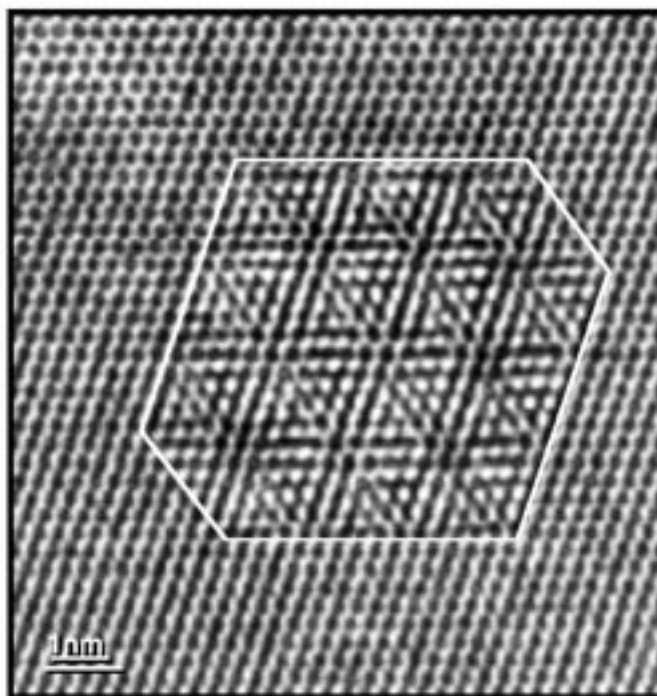
It is now well known that nanostructured materials exhibit many novel, useful, and often exotic properties. However, it is less-widely appreciated that when embedded within a solid, nanostructures may have very different properties. A solid matrix may be used to distribute, orient, or constrain an array of nanocrystals, to isolate them from their environment, or to aid in their synthesis. In turn, a dispersion of nanoscale inclusions has a major effect on the host matrix, an effect that is the basis of dispersion hardening in alloys. Understanding embedded nanostructures is therefore of great fundamental and technological interest.

Unlike free nanocrystals, nanocrystals embedded within a crystalline solid are subject to elastic and crystallographic constraints from the confining solid, which can have a large effect on their behavior. For example, noble gases such as xenon, under confinement in an aluminum matrix can form solid nanocrystals at room temperature. Similarly, while free-metal and semiconductor nanocrystals exhibit a strong depression of their melting point, embedded nanocrystals often show a large superheating that depends on orientation, size, and shape. The size and shape of small inclusions must conform to the embedding matrix: the size must be compatible with the constraints of the two discrete lattices (the inclusion and the matrix, as in Figure 6), and the equilibrium shape must conform to the bicrystal symmetry given by their orientation relationship. In the nanoscale regime, size and shape in turn control the properties. Advances in understanding of the fundamental properties of embedded nanoscale structures opens up opportunities for the discovery of new phenomena and could hold the key to the development of new material.

Nanostructures that are embedded within a solid are of great practical and fundamental scientific importance. Nanoscale precipitates control the strength of all dispersion-hardened alloys such as aluminum- or copper-based alloys, lightweight alloys for energy-efficient transportation, or in some cases high-temperature alloys. Dispersion hardening remains a topic of great importance for materials science. Because of its high spatial resolution, electron microscopy (TEM) is the tool of choice for direct observation of individual nanocrystalline inclusions. However, the environment of solute atoms before or during nucleation of a new phase is not accessible to TEM techniques and hence far less is known about clustering that occurs before the formation of a critical nucleus, which is an embedded nanocrystal. The immediate environment of solute atoms before precipitation is an important unresolved question. The average size, shape, and atomic environment of a pre-precipitation cluster of host-lattice vacancies and solute atoms are of fundamental importance to understanding the nucleation of new phases. Any technique that could shed new light on solid-state nucleation would have a major impact on materials science.

Intergranular films are nanostructures under solid constraint from the adjacent grains in a polycrystalline material. The understanding and control of intergranular films is of tremendous importance for bonding, solidification and sintering of materials. In ceramics, intergranular films control the mechanism of sintering during synthesis and the mechanical, thermal, and electrical properties during service. To understand the relationship between the physical and chemical properties of such films and their constraint in the nanoscale space between solid grains would allow important advances in joining, processing, and performance of ceramics. It would therefore be of great value to determine the structure of such intergranular films, especially at elevated temperatures where their interaction with the adjacent crystals establishes the microstructure.





*Figure 6. Atomic-resolution electron micrograph of lead nanoparticle 5 nm in size (outlined) embedded in an aluminum matrix. Because of constraints from the solid matrix, such embedded nanoparticles follow a magic size sequence, are aligned with the matrix lattice, adopt faceted equilibrium shapes, and superheat by up to 100° C before melting. [Figure courtesy of Uli Dahmen, Lawrence Berkeley National Laboratory.]*

### 2.3.2 Opportunities for Synergistic NCEM/ALS Research

At present, very few investigations take full advantage of the combined characterization capabilities that exist with synchrotron and microscopy facilities. There are many opportunities for such synergistic research wherever the high *spatial resolution* of TEM imaging and the statistically averaged accuracy of x-ray spectroscopy with high energy resolution from x-ray diffraction complement each other. This includes all research where microstructure is important, i.e., most of materials science. An atomic-resolution image of a nanoscale structure is often an invaluable complement to an x-ray study. TEM can resolve structure to the 1-Å level and is excellent for global imaging. However, TEM does not provide good statistics and has only moderate [e.g., 0.5 eV for energy-loss spectroscopy (ELS)] spectral and temporal resolution. Combined experiments using TEM and synchrotron facilities would be of great advantage for understanding surfaces and buried interfaces, defect structures and the mechanisms and dynamics of solid-state phase transformations.

Perhaps the best way to illustrate the synergy between x-ray diffraction techniques and TEM is via the mechanical properties of crystals, which are determined both by a crystal's structure and by its defects. X-ray diffraction is the best tool to determine crystal structure, while TEM excels at determining its defect distribution. Both are necessary to understand the deformation behavior of crystals. A similar synergy exists for many different characteristics of materials, and some specific examples are outlined below.

One of the most important features of engineering materials is the structure of internal or buried interfaces and their defects. Internal interfaces, such as grain boundaries or heterophase interfaces, control the mechanical, magnetic, electrical, and corrosion properties of materials. While the structure of interfaces is responsible for many of their global characteristics, it is the interfacial defects that often control their behavior, in much the same way as dislocations control the mechanical behavior of bulk crystals. Thus, opportunities for combined projects exist in the general area of solid-solid interfaces where synchrotron radiation can solve global structures and TEM can identify the local structure and distribution of defects. The challenge in this field is to match the enormous advances of surface science that were made possible by new surface-science instrumentation and techniques in the last two decades. Solid-solid interfaces may be considered a joining of two surfaces, resulting in phenomena that parallel those of surfaces plus an additional set of new phenomena that result from bi-crystallography (the color crystallography of two single crystals joined with a given orientation relationship). As a consequence, interfaces should exhibit the full array of phenomena now known for surfaces, such as roughening, faceting, premelting, adsorption, and reconstruction, plus a new set of phenomena specific to interfaces, such as translation, dissociation, strain fields, slip transfer, interfacial films, special bonding states, and new features yet to be discovered.

Opportunities for synergistic TEM/synchrotron research extend to the study of dynamic phenomena such as domain motion in ferroelectric, magnetic, or martensitic crystals, and phase transformations, such as corrosion, wetting, or melting. For example, high-temperature, high-resolution TEM is able now to observe a size-dependence of melting in nanocrystalline inclusions. However, the dynamics of this process are beyond the current temporal resolution of the technique, and it is unclear whether the observed effect is due solely to size or also depends on shape. Pulsed x-ray diffraction and spectroscopy resolution would be able to provide complementary accurate information on the melting process with better than nanosecond resolution. Conversely, domain configurations evolving during the growth of magnetic thin films could be followed dynamically in a spin-polarized low-energy electron microscopy (LEEM), while complementary spectroscopic information is obtained by photoelectron electron microscopy (PEEM). This would combine the high spatial resolution and global-imaging capability of electrons with the spectroscopic capability of the ALS and thereby afford a unique opportunity for understanding fundamental questions in the rapidly emerging field of thin-film and surface magnetism.

Other opportunities for the complementary use of synchrotron and TEM facilities exist in the area of defects and their atomic, electronic, and elastic structure. In most circumstances defects control the properties of materials, and it is of fundamental importance to understand their structure. The atomic structure of defects may be solved in some cases by atomic-resolution TEM. By synthesizing model samples containing a high density of similar defects, complementary high-resolution spectroscopic information may be obtained on the synchrotron. Both types of information, atomic and electronic structure, can then be used to refine electronic-structure calculations. Similarly, convergent-beam electron diffraction may be used to map elastic strain fields on the nanometer scale by TEM. Microdiffraction using hard x rays may be used to study the same system on a sub-micron scale. Both types of information, on the sub-micron and nanoscale, are needed in many industrial applications. In crystallographic studies, TEM may be used to characterize the defect structure of crystals whose structure is to be “solved” by x-ray diffraction. In addition, for the study of bonding in crystals, one may use electron diffraction to measure low-order structure factors (where it is more sensitive than x rays), but use x-ray methods to measure the high-order reflections, where they are most sensitive.

### 3. Special Opportunities for Semiconductor Research at the ALS

Eugene E. Haller (leader), Daniel Chemla, and Steven Louie, University of California Berkeley; Joel W. Ager, Michael Martin, Wei Shan, and Wladyslaw Walukiewicz, Lawrence Berkeley National Laboratory

The ALS offers continuously tunable, high-brightness radiation from the infrared through the ultraviolet. The relatively low cost of exploiting this frequency range, together with the broad appeal to researchers in many fields, makes semiconductor research a high priority for the ALS. In the following sections we discuss two especially attractive areas of research that are of current interest and that take advantage of the unique attributes of the ALS.

#### 3.1 Wide-Bandgap Material Studies at the ALS

Optical properties of wide-gap materials present new challenges to researchers who have studied standard semiconductor systems at photon energies below 3.5 eV. “One-electron” (weakly correlated) systems with wide bandgaps include the group III-V nitrides,  $\text{SiO}_2$ ,  $\text{Si}_3\text{N}_4$ ,  $\text{SiC}$ , and  $\text{MgO}$ . Strongly correlated “many electron” systems with wide gaps include  $\text{NiO}$  and  $\text{Cr}_2\text{O}_3$  (discussed in the report of the Working Group on Complex Materials). The properties of these materials are determined by strong electron-electron correlation. Despite the vast number of color-center studies with alkali halide crystals that were performed over 30 years ago, the bulk optical properties of these materials are still poorly understood. In fact, all the wide-bandgap materials have been less well studied than the smaller bandgap materials, in part because of the lack of experimental tools that function in the appropriate spectral range. Optical studies with intense, continuously tunable UV radiation (time resolved as well, for certain experiments) hold great promise for discoveries of new phenomena, new properties, and new device technologies.

##### 3.1.1 Scientific Challenges

Intrinsic properties of importance include fundamental bandgap energy, optical response, band structure, and piezoelectricity. Relevant extrinsic properties include energy levels of dopants and impurities, point and line defects, precipitates and clusters (often on the nanometer scale) and, in alloy systems, alloy composition fluctuations. Recently, the scientific and technical focus in wide-gap materials research has been on the group III-nitrides, wide-gap II-VIs,  $\text{SiC}$ , and diamond. Open scientific questions concerning these materials include:

- Structural instability of II-VI materials under intense UV illumination (diode lasers self-destruct!).
- Effective acceptor and donor doping (in most cases either only acceptors or only donors can be introduced but not both).
- Nature of impurity and defect-induced deep levels.
- Properties of free and bound excitons with small Bohr radii (strongly localized).
- Radiative and non-radiative recombination processes (e.g., Group III-nitride based lasers function in spite of huge defect densities).
- Large red-shift of electroluminescence/photoluminescence (EL/PL) compared to the optical gap in  $\text{InGaN}$ .

##### 3.1.2 Technical/Experimental Challenges

To study these materials, it is necessary to have probe radiation from the far infrared up to and beyond their bandgaps. To study intrinsic properties, infrared radiation is useful to probe the local environments of point defects [spectroscopy of local vibrational modes (LVM)]. Finally, useful

information may be obtained from exciting electron-hole pairs with higher energy, more penetrating radiation (e.g., soft x rays). It is critical to perform these experiments with carefully applied external perturbations. Standard methods that have proved extremely valuable for smaller bandgap materials include pressure (hydrostatic with a diamond anvil cell, uniaxial), temperature (down to liquid helium), and intense light illumination (as in pump-probe experiments). These experiments often require using very small samples, e.g., tens of microns square in a diamond-anvil cell (DAC) of volume  $\leq 10^{-6} \text{ cm}^3$ . Because of small sample sizes, it is highly advantageous to have a strongly collimated light source, as in a synchrotron or laser. Infrared studies of such small samples have not been possible using conventional black-body sources. In addition, some of these perturbations (e.g., hydrostatic pressure) produce large changes in the material's bandgap and intrinsic and extrinsic energy levels. To follow the material's changing properties during these experiments, a tunable UV source is required. For the study of wide-gap materials, it is necessary to have a source that functions well in the range from 3.5 eV to 15 eV. This is beyond the range of most tunable laser sources.

Wide-gap materials also present challenges on the spatial scale. For example, in Group III nitrides, there are quasi-grain structures, phase separation (in alloys), and segregation in epitaxial layers on the sub-micron scale. These affect the optical properties in ways that are not yet understood (e.g., InGaN quantum wells). For this reason, it would be highly desirable to have an intense light source that can be focused to very small spot sizes without losing photon flux.

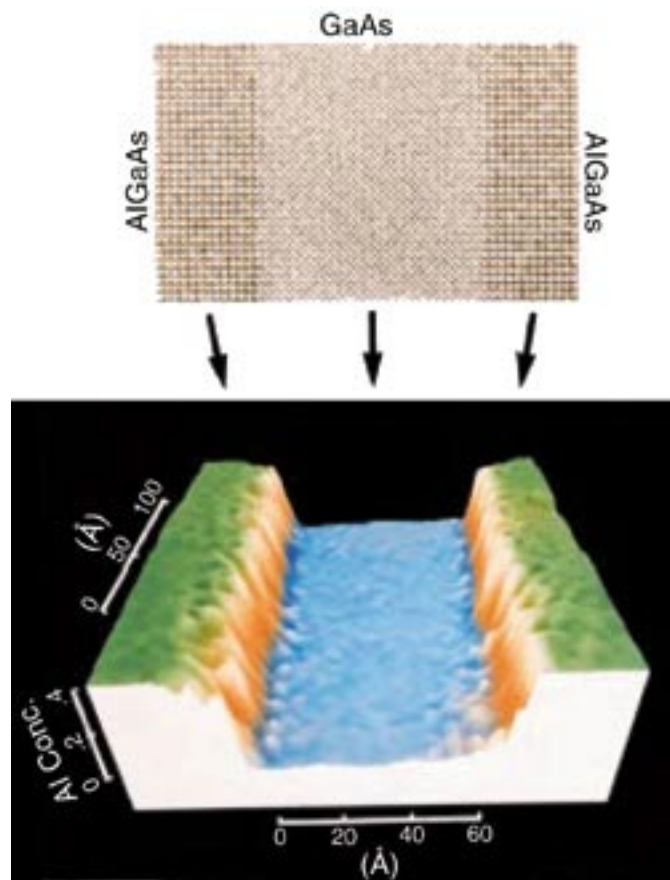


Figure 7. An atomic-resolution electron micrograph of a GaAs/AlGaAs quantum well (top) and the energy landscape seen by an electron in the structure. [Figure courtesy of A. Ourmazd, Institute for Semiconductor Physics, ODER.]

### 3.1.3 Challenges for the ALS

Bright, continuously tunable UV excitation is required for:

- Resonance Raman scattering out to the limit of optical materials, i.e.,  $\lambda \approx 100$  nm or  $h\nu \approx 12$  eV. This would help determine the band structure in wide-gap materials.
- Photoluminescence excitation (PLE) experiments in diamond-anvil cells to 5.5 eV (diamond bandgap). Ordinary laser sources are not easily tunable in this range.
- Origin of large Stokes shift (EL/PL red-shifted from optical gap) in InGaN alloys. (e.g., indium clustering, piezoelectric effects, local stresses).

Small spot size is required for:

- Focused UV plus microscopy [near-field scanning optical microscopy (NSOM)]. Could map variations in bandgap be due to stress or alloy fluctuations?
- Focused x rays for spatially resolved microdiffraction; the relevant length scale is 1  $\mu\text{m}$  and below. Potentially could map grain structure in Group III nitride epitaxial layers.
- Focused IR microspectroscopy for “optical” conductivity and local vibrational-mode studies at high pressures.

Short pulses (sub-100-ps) of tunable UV and soft x rays are required for:

- Time resolved photoluminescence (UV, soft x-ray).
- Transient photoconductivity with tunable radiation using the time structure of ALS radiation (UV, soft x-ray). Carrier dynamics in wide-gap materials (e.g., the effect of “grain structure” on mobility and lifetime in GaN and associated alloys).

And infrared (IR) beamlines are needed for:

- Spectroscopy of local vibrational modes (LVM) with very small samples (10  $\mu\text{m}$ ) under large hydrostatic pressures.
- Spectroscopy of shallow donors and acceptors with very small samples (10  $\mu\text{m}$ ) under large hydrostatic pressures.
- A diffraction-limited beam of IR radiation is ideally suited for the above-listed studies of micro- and nanocrystals because of its high brightness.

## 3.2 Far-Infrared Studies in Very-High-Pressure Diamond-Anvil Cells at the ALS

The application of large hydrostatic pressures in combination with infrared spectroscopy provides a powerful combination of controlled external perturbation and spectroscopic analysis of modern solids. The value of using large hydrostatic pressures in materials analysis is obvious for materials which are used in high-pressure applications. However, high pressures offer significantly more. For example, the band structure of GaAs changes with hydrostatic pressure in the same general way as when GaAs is alloyed with AlAs at ambient pressure. The band structure of AlGaAs with one percent AlAs corresponds to the band structure of the pure GaAs under 1 kbar hydrostatic pressure. This behavior is observed for many crystalline solids and it is of powerful predictive value for alloy design as well, as for the detailed understanding of thermal, electronic, and mechanical properties.

Large hydrostatic pressures can be produced conveniently in a diamond-anvil cell. Consisting of two jewelry-grade diamonds with their tips ground off, it can produce very large hydrostatic pressures of up to 550 GPa ( $\approx 5.5 \times 10^6$  atmospheres) by compressing the small volume formed by a hole in a metal gasket. The diamonds are close to ideal transmitters of electromagnetic radiation from the far infrared to the deep ultraviolet. Samples studied in diamond anvil cells are typically small, a few tens to hundreds of microns in



diameter and a few tens of microns thick. This relatively small sample size poses severe limits on optical studies of properties of solids in diamond anvil cells, especially in the mid- and far-infrared range of the electromagnetic spectrum, which is characterized by weak broadband sources and severe throughput problems. It is only very recently that local vibrational modes of impurities in crystalline solids have been successfully studied as a function of hydrostatic pressure in diamond-anvil cells [see for example “Formation of a DX Center in InP Under Hydrostatic Pressure,” J. A. Wolk, W. Walukiewicz, M. L. W. Thewalt, and E. E. Haller, *Phys. Rev. Lett.* **68** (1992) 3619].

The unique opportunities offered by optical studies of solids under very large hydrostatic pressures will be extended to ever smaller and purer structures, particles of solids so small that a large fraction of all the atoms in one particle are part of the surface. The band structure, melting point, dopant energy levels, defect structures, and several other properties of such small particles have been shown to deviate significantly from bulk properties. The exploration of the mid- and far-infrared properties, especially of impurities and defects (vacancies, interstitials, etc.) in very small particles, offers a broad and most promising field of materials studies that has remained largely unexplored because of usual limitations encountered in the far infrared, including weak sources, throughput problems, and detectors.

A diffraction-limited beam of infrared radiation from the ALS is ideally suited for the studies mentioned above because of its high brightness. The small product of the beam area and solid angle allows a significantly larger number of far-IR photons to pass through a sample in a diamond-anvil cell than from a standard far-IR source. The blackbody equivalent temperature of the ALS beam has been estimated to be of the order of 200,000 K averaged over all the electron buckets in the beam and it approaches 700,000 K in the buckets. These high source temperatures combined with the broad tunability make the ALS an IR source of unprecedented performance.

In order to exploit these extraordinary ALS IR-source properties, we plan to use the two FTIR spectrometers that are currently commissioned at Beamline 1.4. One of the spectrometers (Bruker IFS66v/s) has an unapodized maximum instrumental resolution of  $0.125\text{ cm}^{-1}$  and operates in a vacuum. It belongs to a family of second-generation instruments used worldwide in materials, solid-state physics, and chemistry research facilities. In addition to the mid-IR standard KBr:Ge beam splitter, the spectrometer will be equipped with a set of mylar beam splitters that allow operation in the far IR from  $50\text{ cm}^{-1}$  to  $1,000\text{ cm}^{-1}$  and a quartz beam splitter to allow visible-light spectroscopy from  $8,000\text{ cm}^{-1}$  to  $25,000\text{ cm}^{-1}$ . The second FTIR set-up, a Nicolet 760 instrument with a Nic-Plan IR microscope, has already demonstrated a  $10\text{-}\mu\text{m}$  spot size in the mid IR, which is sufficient to perform microscopy of small samples in diamond-anvil cells.

In order to reduce background radiation, a majority of far-IR spectroscopic studies are performed at low temperatures. The cryostat can also accommodate diamond anvil cells of various designs. We propose to equip the facility with two commercial cells for general use. In addition, cells will be fabricated at Berkeley by several groups with extensive experience in the design and manufacture of such cells.

The choice of detectors to accommodate the various wavelength ranges and the widely varying photon-flux conditions requires special attention. In addition to the proposed set of commercial detectors, we foresee an intensive development effort for new, well-matched IR-detection devices. Again, there exists broad local experience in semiconductor- and superconductor-based IR detectors. For example, the first successful study of local vibrational modes of silicon donor impurities in GaAs under high pressure was performed with a copper-doped germanium photoconductor that was built and integrated with the diamond-anvil cell at the University of California, Berkeley. It is anticipated that this new IR facility at the ALS will stimulate highly interactive and fruitful collaborations between experts in the spectroscopy of solids, in materials properties, and in detector physics and technology.